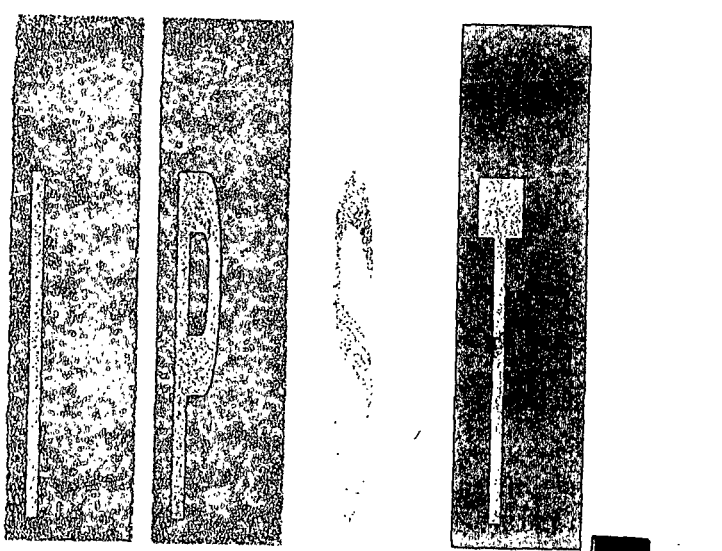
Institute of Paper Science and Technology

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

December 12, 1990



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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

December 12, 1990

CHEMICAL PULPING AND BLEACHING PROJECT ADVISORY COMMITTEE

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November 27, 1990

CHEMICAL PULPING AND BLEACHING PROJECT ADVISORY COMMITTEE DECEMBER 12, 1990 AGENDA

8:45	*Introductions*	
9:00	*Role of PAC Committees*	*Yeske*
9:30	*Antitrust Regulations and Confidentiality of Staff Reports*	
9:45	*Nature of the Information Exchange at Meetings* *a. Information vs Formal Presentations* *b. Detail vs Overviews* *c. Committee Member Reporting Responsibilities to Chairman*	
10:00	*Frequency and Location of Meetings*	
10:05	*Break*	

PROJECT REPORTS BY STAFF

10:20	*Project 3661*	*Dimmel*
10:50	*Project 3475*	*Dimmel*
11:00	*Project 3524*	*Ragauskas*
11:30	*Project 3477*	*Banerjee*
12:00	*LUNCH*	
1:00	*Project 3474*	*McDonough*
1:45	*Project 3534-43*	*McDonough*
2:00	*Project 3684*	*Sonnenberg*
2:30	*Project 3685*	*Dimmel*
3:00	*Committee Feedback*	
3:30	*Next Meeting Date*	
3:35	*Adjourn*	

TABLE OF PROJECTS

TABLE OF PROJECTS (CONTINUED)

Project 3699

EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS

Start: 5/90	*End: 12/91*	*Courchene*	*$55,000*

Project 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

Start: 1979	*End: Indefinite*	*McDonough*	*$250,000*

Project 3534-43 (CKPG)

ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMICHEMICAL PULPING

Start: 9/4/90	*End: Indefinite*	*McDonough/Woitkovich*	*$5,000*

Project 3675

EFFECTS OF BLEACHING PROCESS CHANGES ON ORGANIC CHLORINECOMPOUNDS IN EFFLUENT AND PULP

Start: 6/89	*End: 7/90*	*McDonough/Woitkovich*	*$?*

Project 3684 (API/NCASI FUNDED)

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION
PART I: PRECURSOR FORMATION AND REACTIVITY

Start: 9/89	*End: Indefinite*	*Sonnenberg*	*$89,000*

Project 3685 (CHLORINE INSTITUTE FUNDED)

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II:
CHLORINATION AND DIOXIN REACTIONS

Start: 7/1/90	*End: 6/31/91*	*Dimmel*	*$180,000*

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3661

SULFUR-FREE SELECTIVE PULPING PROCESS (DOE FUNDED PROJECT)

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3661: SULFUR-FREE SELECTIVE PULPING PROCESS (DOE FUNDED PROJECT)

PROJECT LEADER: Donald R. Dimmel

IPST GOAL:

Improved process for bleached chemical pulps.

OBJECTIVE:

To develop a sulfur-free pulping process based on conversion of lignin to pulping additives which will increase delignification rates and decrease the degradation of carbohydrate fibers.

CURRENT FISCAL YEAR BUDGET: $207,700

PRIOR RESULTS:

A process is under development to provide low-cost anthraquinone catalysts from lignin which will lead to improved chemical pulping. For the last two years, our research has been supported by the Department of Energy. Our research team consists of: Patricia Caldwell and Alison Daube (technicians), Dr. Ken-ichi Kuroda (visiting scientist), and Dr. Earl Malcolm (research division director) from IPST; Dr. Joseph Bozell and Dr. David Johnson (senior organic chemists), Dr. Helena Chum (manager of the Chemical Conversion Branch), and Ms. Bonnie Hames (staff member and graduate student) from SERI; Mr. Arthur Power, an independent consulting process engineer, on the economic evaluations.

The research, which has focused on both the scientific and economic aspects of commercialization of an AQ-from-lignin process, has been divided into two large stages, lignin processing and chemical processing.

The lignin processing stage involves selectively isolating a low-molecular-weight fraction from a lignin source. [The processing of a whole lignin is unattractive because of expected non-productive consumption of chemicals.] Two methods for separation of this low-molecular-weight fraction have been evaluated. Supercritical fluid extraction of a pulping liquor after precipitation of the bulk lignin displays good selectivity for low-molecular-weight lignin, but the yields are low. Simple organic solvent extraction of organosolv lignins is less selective but provides large amounts of low-molecular-weight material. Organosolv lignin appears to contain a higher proportion of the low-molecular-weight lignin which resembles native lignin more closely than other types of lignin, such as kraft.

The chemical processing of the low-molecular-weight lignin contains two critical chemical steps: (1) the lignin is treated with an inexpensive oxidizing agent to give a mixture of methoxy-substituted benzoquinones and (2) the benzoquinones are converted into nonaromatic anthraquinone precursors by treatment with a diene, using the well-known Diels-Alder reaction. Final conversion of these precursors to anthraquinone derivatives occurs by loss of methanol and hydrogen, either during reaction or in a separate step. The aromatization step may be unnecessary; partially aromatic anthraquinone also functions as a pulping catalyst by in situ conversion to anthraquinone.

The single most important determining factor in the final cost of anthraquinone prepared from lignin is the overall yield of the chemical processing steps and, consequently, this is where our recent activity has been focused. An economic evaluation determined that the anthraquinone cost drops exponentially with increasing overall yield. A number of oxidizing agents have been evaluated for suitability in the first step of the chemical processing stage. Because of the structural complexity of lignin, initial work was performed on compounds that model lignin's behavior. Fremy salt is an excellent oxidant for the production of benzoquinones from phenols which bear lignin-like functional groups; however, the reagent does not appear suitable for a large industrial process.

Hydrogen peroxide oxidation of certain lignin models to give benzoquinones has been optimized to give yields of 80-90%. However, a large excess of oxidant is needed for good yields, thereby reducing its cost-effectiveness. Also, the yields of benzoquinones from H_2O_2 treatment of isolated lignins have been discouragingly low. These drawbacks have led to the examination of other oxidants.

Nitrogen dioxide, a readily available material, has been shown to be an effective oxidant for lignin models. The procedure involves treating the substrate at room temperature with NO_2/O_2 in an alcohol solvent. The yields of dimethoxybenzoquinone with simple lignin models are often above 80% and with an extracted lignin in the 20-40% range.

In addition, inexpensive oxygen has been successfully used as an oxidant in the presence of catalytic amounts of certain transition metal complexes. Yields of benzoquinones from the oxidation of lignin models as high as 85% have been realized under mild conditions.

The second step in the chemical processing, addition of a diene to the benzoquinone mixture to give anthraquinone precursors, has been demonstrated for each of the benzoquinones expected from lignin oxidation. The yields of these reactions can be high, especially for formation of one ring. However, the formation of two rings simultaneously (benzoquinone directly to an anthraquinone) is a more difficult task; the intermediate naphthaquinone structures react very slowly under standard conditions. Recent encouraging results, using catalysis to assist the diene addition and a novel diene addition reaction carried out in water, suggest that a direct one-step conversion of benzoquinones to anthraquinones, without isolation of non-aromatic precursors, is possible. We now suspect that the Diels-Alder step will not be a significant contributor to the overall process cost.

The research work of John Wozniak (Ph.D. 1988, IPC) demonstrated that pulping catalysts can be prepared from lignin and lignin-derived chemicals. The aromatic rings of lignin were oxidized to benzoquinones, which in turn were modified by Diels-Alder reactions into anthraquinone type pulping catalysts. The synthetic yields achieved by Wozniak were respectable; the Diels-Alder products had moderate to excellent pulping activity. The process (lignin--catalysts) has potential for providing an inexpensive, selective, sulfur-free pulping process.

The oxidative procedures developed by Wozniak were reexamined in an attempt to develop accurate yield measurements when employing small sample sizes. Both peracetic acid and peroxide oxidation procedures, when applied to small samples, gave inconsistent results with gas chromatography (GC) analysis. High water solubility and volatility make the product analysis difficult by GC. Therefore, liquid chromatography (LC) was turned to as a method of analysis. Derivatization and solvent changes are necessary for this technique. Starting materials and product components have been shown to separate well by LC. Treating the product mixtures with iron salts converts hydroquinones to quinones and simplifies the product analysis.

SUMMARY OF RESULTS SINCE THE LAST REPORT:

Considerable time has been devoted to putting data together, writing a 60-page annual report to DOE, and writing up research procedures, etc., by Dr. Karim and Pat Van Vreede, both of whom left IPST in September.

Research has continued on optimizing the yields of benzoquinones by NO_2/O_2 oxidation of lignin and lignin model compounds. About 40% of the syringyl units in an extracted (lower molecular weight) organosolv aspen lignin were converted to dimethoxybenzoquinone. Yields of 80% have been shown with syringyl alcohol. The yield of dimethoxybenzoquinone (DMBQ) progressively increased during the first 8 hours and then leveled off at 15% (our best yields yet) when White Oak organosolv lignin was treated with NO_2/O_2. The yields in the presence of NHS are typically 1-1.5% higher than in the absence of NHS. The yields of monomethoxybenzoquinone (MBQ) were consistently low - less than 1%. The stability of MBQ to NO_2/O_2 was checked; it showed no significant loss after 1-1/2 hours, 20% loss after 3 hours, and 77% loss after 20 hours of treatment.

The oxidation of syringyl alcohol by NO_2/O_2 in various solvent systems and lengths of time has been extensively investigated. Methanol proved to be the superior solvent for DMBQ production. The stability of DMBQ was good for all solvents tested.

The reactions of potassium dichromate with selected lignin model compounds and lignin were also examined; yields of DMBQ in the 10-55% range for models and 1.2% for a hardwood kraft lignin were not encouraging enough to pursue further. No formation of MBQ was observed. The yields of benzoquinones from oxidations of the same lignin done with H_2O_2/NaOH gave about 1/4 the yields of NO_2/O_2. No further work is planned for the direct generation of benzoquinones by H_2O_2/NaOH oxidation.

Degradation of lignin into smaller fragments before performing NO_2/O_2 oxidation should result in higher yields of benzoquinones. Three lignin pretreatments were examined: (1) H_2O_2/NaOH oxidation, (2) acidolysis, and (3) H_2O_2/NaOH oxidation after acidolysis. The H_2O_2/NaOH oxidation may lead to side-chain cleavages and to the formation of hydroquinones via Dakin-like reactions. Acidolysis was expected to yield lignin enriched in lower molecular weight fractions, containing higher levels of phenolic, a-carbonyl and conjugated double bond groups, all of which should be susceptible to peroxide degradation. Both peroxide and acidolysis were the effective treatments; the combination of the two is in progress. The effects of the pretreatments on this particular lignin on the DMBQ yield were: acidolysis (10.7%), H_2O_2 (5.0%), and no pretreatment (3.3%). In all experiments, the yields of monomethoxybenzoquinone were only a trace.

The research results of an IPST M.S. student in the area of aqueous Diels-Alder reactions of the benzoquinones to give anthraquinones, have been extended by project staff. We examined several factors related to optimization of yields, both in pure water and mixed water/organic solvents. Additional studies are needed in this area. A large scale Diels-Alder reaction has been performed. The product mixture, which contained oil from the high temperature bath, was purified by chromatography. The resulting mixture was added to pine chips (0.1%) and pulped under standard soda conditions. In comparison to three control soda/AQ cooks, the Diels-Alder mixture was close in activity to a 0.1% level AQ.

Dr. Joe Bozell at SERI has found that Diels-Alder reactions of benzoquinones on solid surfaces give high levels of anthraquinone; he will be pursuing this area in much greater depth.

A meeting between Stan Sobczynski, the SERI research team, and me occurred on August 14, to review our accomplishments and present research plans for a continued DOE support beyond the initial 3-year funding period.

PLANNED ACTIVITIVIES THROUGH FISCAL YEAR 1991:

We have demonstrated the feasibility of each step in the overall process under certain cost constraints. The objective of our near future research is to develop and optimize our lignin extraction and chemical conversion efficiencies to further lower the cost of pulping catalysts from lignin. We will be looking at a new organosolv process being developed at SERI for its ability to produce low-molecular-weight lignins and ways to take any type of lignin down to small fragments for efficient conversion to catalysts. Continued research will be directed on methods to oxidize lignin and perform high yield Diels-Alder reactions of benzoquinones on solid surfaces and in aqueous media.

POTENTIAL FUTURE ACTIVITY:

The research will move the successful results of the laboratory research to larger scale.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3475

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3475: FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

PROJECT LEADER: Donald R. Dimmel

IPST GOAL:

Improved process for bleached chemical pulps.

OBJECTIVE:

Provide a fundamental understanding of the chemical and physical reactions that control both:

(1) the rate of lignin removal, hemicellulose dissolution, and cellulose degradation, and

(2) the structures of the lignin, hemicelluloses and cellulose that remain in the pulp after pulping and bleaching.

CURRENT FISCAL YEAR BUDGET: $120,000

PRIOR RESULTS:

The detailed mechanistic studies of pulping delignification chemistry conducted in this project have led to a greater understanding of the factors which control lignin fragmentation and condensation reactions. A significant portion of the research was directed towards understanding the reactions of anthrahydroquinone (AHQ) with lignin substrates. Our interest here relates to the fact that anthraquinone (AQ) pulping systems show improved selectivities. The research, including related student work has led to over 30 publications in the last 10 years, with several additional articles submitted and in preparation.

The project has also been concerned with understanding the chemistries associated with carbohydrate chain cleavage reactions that occur during alkaline pulping and bleaching. Such reactions cause a lowering of the degree of polymerization (DP) and thus a loss in paper strength properties. Changes in DP are seen by changes in pulp viscosities and molecular weight distributions. Earlier work in this project involved developing a GPC method of obtaining cellulose molecular weights.

Research activity in the past few years has concerned comparing the reactivity difference of amorphous and crystalline cellulose samples; any observed difference should reflect the importance of "physical effects" in carbohydrate chain cleavage reactions. A relatively high viscosity amorphous cellulose sample and a crystalline cellulose sample have been prepared from cotton linters. The samples were reduced with sodium borohydride ($NaBH_4$) to prevent "pealing" losses in monomer units when heated in alkali. The viscosity losses as a function of time during simulated alkaline pulping followed the order: amorphous > cotton linters > kraft pulp > crystalline cellulose. The rate of DP loss was further increased slightly when amorphous or crystalline cellulose was heated in alkali in the presence of AQ.

Similar reactivity trends were observed for the various cellulose samples in a simulated oxygen-alkali bleaching reaction at 100°C and a hydrogen peroxide bleaching reaction at 50°C and pH 11. The viscosity losses for amorphous cellulose in oxygen-alkali were inhibited by the presence of magnesium. The addition of cobalt, above a level of 0.162 mole $CoSO_4$/100 g of cellulose greatly accelerated the amorphous cellulose viscosity losses. The combination of Mg and Co was even more harmful to the sample's viscosity. Treatment of cotton linters and amorphous cellulose with SO_2 to remove metals caused no loss of viscosities at pH 2.3; however, at pH values below 2.3, large viscosity losses were observed. A combination of added magnesium sulfate and sodium silicate prevented viscosity losses during hydrogen peroxide reaction with the amorphous cellulose.

Several detailed oxygen-alkali/cobalt studies of viscosity changes with crystalline, amorphous, and kraft celluloses have been performed by different researchers in our laboratory. The magnitude of the reactivity differences varies with researcher and newly prepared samples. For example, the magnitude of viscosity losses at early reaction times for the kraft and highly crystalline cellulose have been observed to vary. The viscosity treads towards the end of a treatment increased slightly for one of our researchers. Nevertheless,it is apparent that highly crystalline cellulose samples and kraft pulp degrade much more slowly than amorphous cellulose under pulping and bleaching conditions.

SUMMARY OF RESULTS SINCE LAST REPORT:

Previous samples of crystalline, amorphous cellulose, and the shredded cotton linters, from which we made the other cellulose samples, deteriorated during the year. They had been stored "open" in a vacuum desiccator; the house vacuum apparently produced water in the line on occasion. New batches of amorphous and crystalline cellulose were prepared; the viscosities of each sample was equal to or better than previous samples. However, this batch of amorphous cellulose appeared to be considerably less reactive than earlier ones. For example, when this batch was treated with hydrogen peroxide for various time periods, consistencies, and concentrations, only minor degradation (as noted by viscosity changes) were observed, even though residual peroxide was present in the reaction samples. Degradation was greater in oxygen/alkali runs. A viscosity drop from 40 to 32 occurred in 1 hour with 0.1M $NaOH/O_2$ at 100°C; however, previous amorphous cellulose samples dropped more than 50% under these conditions. The addition of vanillyl alcohol had little effect on the $NaOH/O_2$ degradation rate. A $NaHCO_3/O_2$ treatment at 100°C showed small viscosity decreases; while a Na_2CO_3/O_2 treatment gave moderate decreases.

Many recent attempts to produce amorphous cellulose have failed due to incomplete dissolution of the cotton linters in the cellulose solvent. However, when the mode of heating was changed and a second addition of DMSO, SO_2, and diethylamine was made approximately one hour after the first addition, the linters completely dissolved, giving amorphous cellulose with a viscosity of 25.2 c.p.s. New samples of crystalline cellulose and cotton linters were also prepared.

Since leaving Appleton, we have been unable to check the various cellulose samples' crystallinity by X-ray diffraction. Possibly, some of our "amorphous" samples may have contained crystalline components and, thus, been less reactive than earlier samples. Degradation reactions of the new cellulose samples are in progress.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

The large backlog of results of the project's carbohydrate research has been organized in preparation for internal and external publications. Publication of the research results and performing supporting experiments for the publications will be the focus of the fiscal year 1991 activities.

POTENTIAL FUTURE ACTIVITY:

The amorphous cellulose bleaching chemistry studies could be expanded to examine (1) additional chemicals (ozone, chlorine dioxide, etc.), (2) process variables, (3) the influence of selected metals and "dead load" salt effects, and (4) more detailed molecular weight distributions. The aim will be to develop a fundamental understanding of bleaching chemistry which may lead to better nonchlorine bleaching systems. Research activities involving delignification reactions have been temporarily halted until additional personnel becomes available.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3524

FUNDAMENTALS OF BRIGHTNESS STABILITY

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3524: FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT LEADER: Arthur J. Ragauskas

IPST GOAL:

Increase the usefulness of high-yield fibers.

OBJECTIVE:

Research activities will be directed at investigating the fundamental chemical reactions which are initiated when high yield pulps are photolyzed. The knowledge gained from these studies will be employed to stop or significantly retard the photoyellowing of mechanical pulp.

CURRENT FISCAL YEAR BUDGET: $150,000

PRIOR RESULTS:

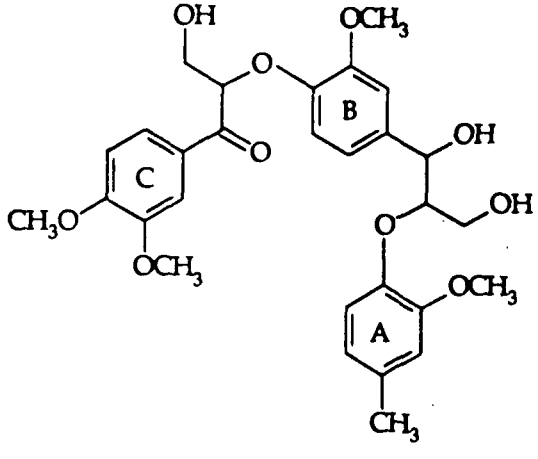
This project was reinitiated with the Institute's relocation to Atlanta. Previous IPST investigations into the fundamentals of brightness stability had examined several parameters involved in the photoyellowing of mechanical pulp. Current research efforts have taken a new approach which employs the use of model compounds to study the brightness reversion phenomena.

SUMMARY OF RESULTS SINCE LAST REPORT:

Quinones appear to be produced during photoyellowing. Their photochemical behavior on a solid matrix may account for color development and is, therefore, being studied in this project. Mono and dimethoxybenzoquinone were synthesized by a unique route in good yield. Both

quinones have been absorbed onto cotton linters and photolyzed. Dimethoxybenzoquinone was relatively stable to the photolysis conditions. Photolysis of monomethoxybenzoquinone yielded several products, with the predominant compound being the hydroquinone. The photoreduction of monomethoxybenzoquinone suggests that the cellulose is in turn oxidized during the photochemical reaction. Research efforts are currently focused on characterizing this reaction sequence and identifing other minor components formed during the irradiation process.

The photolytic behavior of large lignin models absorbed on linters is also of interest. Synthetic efforts have led to the production of the A/B portion of the desired trimer shown below.



Research activities are ongoing to couple the final "C" ring onto the A/B dimer.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

Research efforts are to be directed at preparing and photolyzing a series of lignin model compounds believed to be involved in the brightness reversion process. Synthetic endeavors will be focused on completing the vanillin and syringyl trimer model compounds. The photolytic behavior of these compounds, adsorbed onto a solid support matrix will be investigated. Exploratory studies will be directed at preparing a series of *ortho*-quinones that modeled structures proposed to be formed during the photolysis of mechanical pulp.

The photolytic and chemical behavior of *para*-quinones, absorbed onto a solid support matrix will be further explored. The photolysis experiments will be performed on several solid support materials (i.e., cotton linters, mechanical pulp, simple sugars) so as to determine if the support matrix can influence the reaction profile.

FUTURE RESEARCH ACTIVITY:

Future research studies are to be directed at preparing and photolyzing other lignin model compounds (i.e., conjugated olefinic compounds, catechol derivatives,...) believed to be involved in the brightness reversion process. Novel and efficient synthetic methods of preparing these structures will be examined when required.

The photoreactivity of quinones, under the brightness reversion conditions, will be further explored. A careful examination of the literature provides extensive examples of the tendency of quinones to undergo solution phase polymerization and photochemical reactions. The extent to which the solid matrix of mechanical pulp could mediate the photochemical reactivity of quinones is currently unknown. The above proposed studies will therefore extend our knowledge of the chemical reactivity of the quinones formed in mechanical pulp.

Previous IPST research efforts demonstrated that derivatization of *ortho*-quinones with trialkyl phosphites could be employed as a means of detecting *ortho*-quinones in mechanical pulp, by means of ^{31}P NMR. This technique will be employed in this proposed study. The use of solid-state ^{13}C CP-MAS NMR will also be explored to investigate the chemical structure of mechanical pulps and its relevancy to the photoyellowing phenomena.

It is anticipated that the results of the modeling studies will further refine our understanding of the brightness reversion process. These results will then be corroborated with accelerated brightness reversion studies on mechanical pulp handsheets.

Collectively, these investigations will provide fundamental information as to what is occurring in the chemically complex structure of mechanical pulp when it is irradiated. Based upon these studies, novel methods of retarding or stopping the brightness reversion process will be proposed and investigated.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3477

DEVELOPMENT OF NEW ANALYTICAL METHODS

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3477: DEVELOPMENT OF NEW ANALYTICAL METHODS

PROJECT LEADER: Sujit Banerjee

IPST GOAL:

Develop an in-house technique for identifying and quantitating unknown components in mixtures from their infra-red spectra.

OBJECTIVE:

To develop new analytical methodology for paper industry applications.

CURRENT FISCAL YEAR BUDGET: $15,000

PRIOR RESULTS:

Program Area

Reduced Operating Costs, Product Quality.

Accomplishments to Date

Infra-red spectroscopy is used extensively in the industry to identify and quantify resins, extractives, pitch, etc. Owing to signal overlap, identification is frequently impossible if a complex mixture of components is present. We have developed a new method of signal processing whereby components in a mixture can be simultaneously identified and quantitated from the overall infra-red spectrum. The method is being evaluated after which it will be coded into a computer program for automated use.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3699

EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS (API/MTC FUNDED)

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3699: EVALUATION OF COMMERCIALLY AVAILABLE CONDUCTIVITY SENSORS

FUNDING SOURCE: AMERICAN PAPER INSTITUTE - MEASUREMENT TECHNOLOGY COMMITTEE (API-MTC)

PROJECT LEADER: Charles E. Courchene

OBJECTIVE:

To evaluate commercially available conductivity sensors for their ability to accurately and reproducibly monitor alkali concentration in process streams.

CURRENT FISCAL YEAR BUDGET: $55,000

PRIOR RESULTS:

Previous studies as reported in the literature have shown a good correlation between alkali concentration and conductivity. One study done by IPST established relationships of the output of a four electrode sensor and alkali concentration, organic salt concentration, and temperature.

All previous studies have utilized one sensor type or a laboratory instrument. The objective of this project is to evaluate several different sensor types that are presently available under the same conditions. The sensors and transmitters are to be operated in the manner recommended by the suppliers and the process conditions will be established to simulate mill conditions as closely as possible.

The primary variables for the first phase of the study will be temperature, chemical concentration, and flow velocity.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1990:

Installation of a test stand using the Institute's 1.8 cu. ft. digester and circulation pump has been completed. Three types of sensors have been procured on a loan basis from suppliers. These are a four electrode type, an insertion electrodeless type, and a flow through electrodeless type. Instrumentation for flow, temperature, and pressure measurement is also installed in the flow loop.

Phase I testing will use simulated white liquor at typical mill concentrations and temperatures. The response of each sensor will be monitored against the variables being studied. Appropriate relationships will be developed for each sensor and variable.

Testing to date has used pure alkali solutions to check out the factory calibration of each sensor and evaluate the temperature compensation feature of each transmitter. Data collected for each sensor has been sent to the respective supplier for comment.

Testing will continue with the simulated white liquor. Future testing will involve cooking liquor and black liquor as well as the long term stability of the sensors.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3474

ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3474: ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED PULP

PROJECT LEADER: Thomas J. McDonough

IPST GOAL:

To improve the process of production of bleached chemical pulp to make it more compatible with the environment.

OBJECTIVE:

To define pulping and bleaching technology that will decrease or eliminate the need for chlorine in the bleaching sequence.

CURRENT FISCAL YEAR BUDGET: $250,000

PRIOR RESULTS:

Results obtained since the inception of this project are summarized in the September 6, 1988 Status Report. They include empirical optimization of kraft and alkaline sulfite-anthraquinone processes for pulping to low kappa numbers, and studies of methods for reducing chlorine use by making oxygen delignification more selective or by applying hydrogen peroxide.

Formation of dioxins and AOX during bleaching were studied and a particular combination of control measures was shown to be effective. Analytical procedures for AOX were implemented, effects of method parameters were briefly studied and the precision of the method was determined.

Several pretreatments for improving oxygen stage selectivity have been studied. These include nitrogen dioxide, chlorine and bromine. Nitrogen dioxide pretreatment has been studied, not to develop it as a process per se, but rather to understand why it is so effective. The intent is then to use this information in selecting or designing a better pretreatment.

Nitrogen dioxide was shown to react readily with models for lignin units containing free phenolic hydroxyl groups, but sluggishly or not at all with etherified units. Aliphatic hydroxyl groups in the α-position of the side chain were oxidized to carboxyl groups, side chains were displaced and side chain cleavage was also observed. These observations suggest a mechanism that involves lignin depolymerization by side chain displacement and/or ring cleavage, combined with sensitization to oxygen and alkali by incorporation of α-carbonyl groups. Another likely possibility is an increase in alkali solubility of the lignin by incorporation of carboxyl groups.

SUMMARY OF RESULTS SINCE LAST REPORT:

Pretreatments for Oxygen

Mr. Kyle Reed has joined IPST as an Assistant Scientist and has assumed responsibility in this area. Much of his work to date has consisted of acquiring familiarity with, and improving, techniques and equipment.

The current strategy is to determine the effect of selected, specific types of changes in the chemical structure of the residual lignin in unbleached pulp on subsequent oxygen bleachability. These will include separate determinations of effects of carbonyl groups, α-carboxyl groups and demethylation. Work is in progress to determine the effect of NO_2 application treatment on carboxyl content and to attempt to correlate carboxyl content with oxygen bleachability. To further test this correlation, carboxyl content will be increased by pretreatments with oxidizing agents (ozone, peracetic acid, ClO_2, H_2O_2, etc.) and the effect on oxygen bleachability determined.

A series of NO_2 treatments at varying levels of NO_2 application has been completed and oxygen bleaching is in progress. Analysis of the NO_2 stage effluents has shown a linear increase in absorbance at 280 nm with increasing NO_2 application. Thin layer chromatography of effluent extracts shows one major component that may be 2,4-dinitroguaiacol.

Dioxin Formation During Bleaching

Recent work has focused on the effects of mixing and consistency on the level of dioxins formation. Chlorinations were performed at 4 and 6% consistency under conditions of good mixing and poor mixing. The identification of good mixing and poor mixing conditions required development of a method to measure degree of mixing. The method consisted of injecting a solution of phenolphthalein into an agitated suspension of pulp buffered to pH 10. After mixing was terminated, multiple small samples of the liquid phase were withdrawn with a syringe and the dye concentration was specbiophotometrically determined.

The 2 x 2 factorial chlorination experiment was completed in duplicate. Effluent samples from both the chlorination and caustic extraction stages were submitted for AOX and dioxins analysis. The chlorinated pulp was also submitted for dioxins analysis. Both kappa number and viscosity were significantly lower after the well-mixed experiments than after the poorly mixed ones. We are currently awaiting results of the AOX and dioxins analysis.

Labeled Precursor Experiments

A collaborative effort among the Analytical, Wood Chemistry and Pulping and Bleaching Groups is using radioactively labeled DBD to determine whether this dioxin precursor is destroyed by ClO_2.

Spiked pulp was reacted with ClO_2 at 2% consistency and the whole suspension extracted with CH_2Cl_2. The recovery of DBD by counts was 28% and by HPLC 18%. In a control experiment, using pure water instead of ClO_2 solution recovery by counts was 35% and by HPLC 34%. Extraction of the pulp and water phases separately gave 99% recovery of DBD.

These experiments tentatively suggest that DBD is partly destroyed by ClO_2 and that DBD is tightly bound by pulp in aqueous systems. The latter observation may have implications with regard to the accessibility of DBD and its ease of conversion to PCDD's.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3534-43
(CKPG)

FUNDAMENTALS OF SELECTIVITY IN PULPING AND BLEACHING

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3534-43: ESTIMATING YIELD FOR THE PREDICTION OF END-USE PROPERTIES IN SEMICHEMICAL PULPING

PROJECT STAFF: Thomas J. McDonough, Clark P. Woitkovich

IPST GOAL:

Assess the applicability of various nongravimetric techniques to the estimation of semichemical pulp yield. To be addressed exclusively are those methods that show potential in the area of on-line, real-time process control applications.

OBJECTIVE:

Identify the best nongravimetric method of estimating yield in semichemical pulping and develop empirical correlations between yield and product properties. Follow with implementation in an on-line, real-time process control application.

CURRENT FISCAL YEAR BUDGET: $5000 ($75,000 funding by CKPG is expected for calendar year 1991)

PRIOR RESULTS:

Research reported in the literature has suggested several techniques that warrant evaluation as to their suitability in this application. They include near-infrared spectroscopy (NIRS), fluorescence spectroscopy, ultraviolet absorption, total organic carbon (TOC), and refractive index analyses. These methods have all demonstrated potential as indicators of lignin content in pulps and/or pulping liquors. Efforts to date, however, have focused almost exclusively on kraft pulps of relatively low yield and the applicability of these techniques to high-yield pulping remains uncertain.

Exploratory work has focused on the NIRS technique and has demonstrated significant differences between absorption spectra acquired from pulps cooked to 74.7 and 82.7% yield levels. The spectral variations seem most evident when the samples are presented in a dry handsheet form. Similar, less pronounced differences are also evident with wet, fluffed pulp.

PLANNED ACTIVITY THROUGH CALENDAR YEAR 1991:

1. Prepare semichemical pulps in the laboratory that span the yield range typically encountered in the mill. Determine actual yields gravimetrically.

2. Evaluate the usefulness of the above mentioned techniques for the estimation of yield in the laboratory pulps.

3. Develop correlations between yield, as estimated by the most promising method, and selected physical properties of the pulp and paper product.

FUTURE ACTIVITY:

This project will emphasize development of an on-line control strategy for estimating yield in high-yield semichemical pulping processes.

POTENTIAL FUTURE ACTIVITY:

Verify the likelihood of success in the mill application of laboratory correlations developed between control measurements, pulp yield, and product strength properties.

Further develop the control model by defining and incorporating the effects of different raw materials and different pulping conditions on the observed correlations.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3675

EFFECTS OF BLEACHING PROCESS CHANGES ON ORGANIC CHLORINE COMPOUNDS IN EFFLUENTS AND PULP

(Privately Funded Contract Research
Presented with Cooperator's Permission)

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3675: EFFECTS OF BLEACHING PROCESS CHANGES ON ORGANIC CHLORINE COMPOUNDS IN EFFLUENT AND PULP (Privately Funded Contract Research Presented with Cooperator's Permission)

PROJECT LEADERS: Thomas J. McDonough, Clark P. Woitkovich

OBJECTIVE:

To study the influence of some specific process changes on the amounts of dioxins and other organic chlorine compounds found in the effluents and bleached pulp from a softwood kraft pulp mill.

RESULTS SINCE LAST REPORT:

The experiments consisted of a set of laboratory bleaching trials that incorporated various combinations of proposed modifications to the C_D-E_o-D-E-D bleached sequence currently used at the mill. The modifications that were evaluated include improved brownstock washing, high chlorine dioxide substitution, the use of hydrogen peroxide in the extraction stage coupled with a low chlorine multiple in the chlorination stage, and the inclusion of an oxygen delignification stage.

The observed levels of TCDD and TCDF were generally low in both effluents and pulps. The effluent TCDD data were consistent with the hypothesis that all variables had beneficial effects, and TCDD in pulp was decreased by improved washing and high substitution. Effluent TCDF was decreased by decreasing the chlorine multiple, but there was evidence that this strategy was not effective after an oxygen stage, probably as a result of the fact that the oxygen stage itself decreased effluent TCDF levels.

Effluent AOX levels were strongly correlated with the charges of chlorine and chlorine dioxide used in the chlorination stage and were beneficially impacted by all the bleaching process changes investigated, with the possible exception of improved washing. The largest single effect was associated with the introduction of oxygen delignification. The lowest bleached pulp AOX levels (determined by combustion of a pulp sample) were observed at low substitution following an oxygen stage.

Untreated combined effluents were evaluated for acute and chronic toxicity effects as observed in minnow and water flea populations. All full-strength, untreated effluents exhibited severe acute toxicity to the water fleas. Acute toxicity to minnows was less severe and, in some cases, absent. Oxygen delignification appears to reduce acute toxicity to both species, although its effect is most noticeable with the minnows.

Due to the severe acute toxicity, meaningful chronic toxicity data for water fleas was unobtainable. Chronic toxicity data for minnows indicates that the use of improved washing along with a low chlorine multiple resulted in the least toxic effluent. Nevertheless, effluent treatment would be required in order to completely eliminate chronic toxicity to fish.

Other, more traditional, effluent parameters were also evaluated. COD and BOD were reduced by oxygen delignification but the effect was diminished when the oxygen stage was preceded by improved brownstock washing. Oxygen delignification was also the most effective strategy in the reduction of effluent color.

The effects of the process modifications on several key physical and optical properties were also evaluated in the study. Yield and printing opacity were unaffected. Final pulp viscosity was positively affected by the use of a low chlorine multiple and negatively affected by oxygen delignification. Pulps generated in a sequence that includes oxygen delignification generally required more energy to refine. Tensile index was adversely affected by high substitution, except after oxygen delignification. Tear index was adversely affected by high substitution and oxygen delignification. The effects of substitution on tear and tensile were unexpected and should be confirmed by additional experiments.

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3684

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART I: PRECURSOR FORMATION AND REACTIVITY (API/NCASI FUNDED PROJECT)

December 12, 1990

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

CHEMICAL PULPING AND BLEACHING

PROJECT ADVISORY COMMITTEE

Project No. 3685

MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II: CHLORINATION AND DIOXIN REACTIONS (CHLORINE INSTITUTE FUNDED)

December 12, 1990

PROJECT SUMMARY FORM

DATE: December 12, 1990

PROJECT NO. 3685: MECHANISMS OF DIOXIN FORMATION IN PULP PRODUCTION PART II: CHLORINATION AND DIOXIN REACTIONS (CHLORINE INSTITUTE FUNDED)

PROJECT LEADER: Donald R. Dimmel

IPST GOAL:

Eliminate or minimize chlorinated dioxins and chlorinated furans in bleached pulp production.

OBJECTIVE:

The production of dioxins during chlorine bleaching is a major concern to the paper industry. The objective of this project research is to develop a fundamental understanding of chemistry which leads to dioxins in bleached pulp, the reactions of dioxins with selected bleaching reagents, and ways to chlorinate pulps without dioxin production. Conditions will be sought that will (a) define the relative importance of different dioxin precursors, (b) determine the reactivity of chlorine with functionalized precursors, (c) selectively chlorinate lignin and not the dioxin precursors, and (d) destroy dioxins in partially bleached pulps. The principle difference between the research of Project 3685 and that of Project 3684 is that chlorination and dioxin will be the focus of the 3685 study. A laboratory (Battelle) that is specif-ically equipped to handle toxic materials, and is capable of performing ultratrace analyses, will be involved.

CURRENT FISCAL YEAR BUDGET: $180,000

PRIOR RESULTS: New project.

SUMMARY OF RESULTS SINCE LAST REPORT:

Laboratory work at Battelle began in late July. Most of the planned experiments involved a very clean system, namely, substrate absorbed onto cotton linters and, hopefully, will provide valuable fundamental information about reactivities without possible by-product problems. The absorbed substrates were dibenzodioxane (DBD), dibenzofuran (DBF), and lignin models. Spiking with a simple substrate onto a "pure" polymer simplifies the analytical procedures and allows a greater number of experiments to be performed at a reasonable cost.

Background levels of DBD and DBF for cotton linters and the solvent extraction procedure have been determined and appropriate DBD/F spike levels established. Reasonable conditions for conducting chlorinations of DBD/F spiked cotton linters were also established. Conditions were selected which should lead to the production of mono - tetrachlorodioxins. Battelle initially examined treating 5 g of (spiked) linters with 0.015 g of Cl_2 in 500 mL of water at room temperature for two reaction times: 10 and 120 minutes. Analysis of the headspace after 10 minutes on unspiked linters showed nearly 50% of the of Cl_2 charge.

Analysis of the initial chlorination experiments of DBD and DBF spiked cotton linters and various controls has produced some unexpected results. Specifically, extraction of selective chlorinated spiked and unspiked linters and solvents has led to substantial quantities of a pale yellow residue which interferes with simple analysis for chlorinated DBD/F compounds. Preliminary results indicate the presence of DBF and chlorinated DBF components in the extracts of the unspiked linters which have been chlorinated. However, the extensive losses of labeled DBD/F internal standards associated with repeated attempts to separate the compounds of interest from the "yellow residue" has shed some doubts on the validity of the results. Simple chromatography through alumina appears to provide a means to clean up the samples. Other appropriate corrective measures are being pursued.

PLANNED ACTIVITY THROUGH FISCAL YEAR 1991:

The chlorinated cotton linters will be examined in greater depth to determine background levels of DBD/F and related chlorinated analogs before proceeding with the 10 and 120 minute chlorinated spiked cotton linters samples and reaction media. Once these analyses prove useful and reliable, Battelle will select the proper chlorination conditions and perform a series of runs to determine chlorine content in DBD and DBF as functions of chlorination time for spiked cotton linters samples.

A selected number of experiments will compare the reactions of unbleached pulps with the model systems to determine the validity of the model systems. Control experiments will (1) compare tetrachloro dioxin isomer patterns at several different absorbed levels of DBD/F on cotton linters and (2) use radioactive tracers to address the validity of comparing reactions of spiked samples with natural samples.

One set of experiments will address the issue of the source of the dioxin precursors. The distribution of mono-, di-, tri-, and tetrachlorodioxins (DBD/F-Cl_x) as a function of chlorination time will be compared for a DBD/F spiked cotton linters sample and an unspiked pulp sample. If the time development profile of the DBD/F-Cl_x components for the two substrates differ substantially, precursors other than DBD/F will be indicated. The profile of tetrachloro isomers for the two samples will also indicate possible sources of precursors and provide an estimate of the relative importance of different precursors.

Another set of experiments will provide rate data for the disappearance of DBD/F-Cl_x (x=0-4) on a lignin-like substrate. Done at different temperatures, the chlorination rate data should provide energies of activation (Ea) for the substrates and, thus, allow one to better control the chlorination process to give greater selectivity for lignin vs. DBD/F. A follow-up competitive experiment will verify the expected selectivities under different chlorination conditions. We will also examine how the selectivity changes with the addition of chlorine dioxide to the chlorination reactions. DBD/F spiked cotton linters, which have been treated with NO_2 or O_2, will be chlorinated to show if substituted precursors will still give rise to dioxins upon chlorination.

Finally, we will treat bleached pulp (which contains trace levels of dioxins) with ozone, peroxide, oxygen, and other possible commercial electrophilic reagents to test the stability of dioxins to various post-chlorine bleaching stages.

POTENTIAL FUTURE ACTIVITY:

This is a one-year funded project.